

Extension of the basis set of linearized augmented plane wave method (LAPW) by using supplemented tight binding basis functions

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In order to increase the accuracy of the linearized augmented plane wave method (LAPW) we present a new approach where the plane wave basis function is augmented by two different atomic radial components constructed at two different linearization energies corresponding to two different electron bands (or energy windows). We demonstrate that this case can be reduced to the standard treatment within the LAPW paradigm where the usual basis set is enriched by the basis functions of the tight binding type, which go to zero with zero derivative at the sphere boundary. We show that the task is closely related with the problem of extended core states which is currently solved by applying the LAPW method with local orbitals (LAPW+LO). In comparison with LAPW+LO, the number of supplemented basis functions in our approach is doubled, which opens up a new channel for the extension of the LAPW and LAPW+LO basis sets. The appearance of new supplemented basis functions absent in the LAPW+LO treatment is closely related with the existence of the \dot{u}_l -component in the canonical LAPW method. We discuss properties of additional tight binding basis functions and apply the extended basis set for computation of electron energy bands of lanthanum (face and body centered structures) and hexagonal close packed lattice of cadmium. We demonstrate that the new treatment gives lower total energies in comparison with both canonical LAPW and LAPW+LO, with the energy difference more pronounced for intermediate and poor LAPW basis sets.

I. INTRODUCTION

The choice of a basis set which may first appear as “the black art” [1] is being constantly debated within the quantum chemistry community. It is well known that in molecular calculations there are two main groups of molecular basis sets introduced by Pople and collaborators (see [1] and references therein) and more recently by Dunning [2]. Both groups supply us with the whole hierarchy of basis sets, where at each step we can enrich the main set by polarization functions of high orbital type or by diffuse functions. For example, one has to add polarization functions if polarization effects are expected to be important, or diffuse functions if we want to refine the description of extended molecular states. Not surprisingly, the actual choice of a basis set depends on the task to be solved and is considered as a difficult problem. For heavy and laborious calculations the choice of a basis set is crucial since on one hand we want to obtain a reliable result and on the other hand minimize the computer time to achieve the goal.

In contrast to this complicated hierarchy of molecular

basis sets, the choice of bases in electronic band structure calculations and here we imply mainly the linear augmented plane wave (LAPW) method [3–5], seems rather simple. The number of augmented plane waves is commonly determined by the parameter $R_{MT}K_{max}$, where R_{MT} is the smallest muffin-tin (MT) radius, and K_{max} is the maximal value of the plane wave vector. The K_{max} value implies that the kinetic energy cut off is $K_{max}^2/2$ (in atomic units). However, in practice some band structure calculations can not be carried out without so called local orbitals (LO) [6]. Such situations occur in systems with semicore electron states which cannot be fully confined within the MT-spheres. The problem of extended core states and its relation to our approach is discussed in detail in the next section. What concerns us here is that the introduction of local orbitals represents an extension of the canonical LAPW basis set albeit the form of new basis states (local orbitals) is very different from the standard augmented plane wave basis function. The LAPW+LO scheme proposed by Singh [7], [6] is practical, but the way it has been introduced is not fully satisfactory. The form of the local orbital functions is not derived from a general approach, and arguments for adding LO basis states are purely variational.

In the present paper we show that the appearance of supplemented basis functions can be understood as a re-

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sult of refinement of the LAPW band scheme when in an effort to increase its accuracy we use two linearization energies (corresponding to two electron bands). We will demonstrate that new basis states are of two types. The first group gives the local orbitals in the form suggested by Sing [7]. however, the basis functions of second type have different form which is not used in the LAPW+LO method. Therefore, the canonical LAPW basis set and also the LAPW+LO basis set can be extended to a more complete basis set. New basis functions and consequences of their introduction are closely examined in the present work.

The paper is organized as follows. We start with revisiting the problem of extended core states which gives rise to the LAPW+LO scheme and formulate our initial statement for the refinement of the LAPW method, Sec. II. In Sec. III we present our method which results in adding tight binding basis functions to the canonical LAPW basis set. In Sec. IV we apply the method to electron band structure calculations of the face centered and body centered lattice of lanthanum and the hexagonal close packed lattice of cadmium. Our conclusions are summarized in Sec. V.

II. THE PROBLEM OF EXTENDED CORE STATES

The linear augmented plane wave (LAPW) method [3–5] is probably the most precise method for electronic band structure calculations and is widely used for the calculation of materials properties [6].

In the LAPW method [3–6] space is partitioned in the region inside the nonoverlapping muffin-tin (MT) spheres and the interstitial region I . The basis functions $\phi_n(\vec{k}, \vec{R})$ where $n = 1, 2, \dots, N$ are given by

$$\phi_n(\vec{k}, \vec{R}) = \begin{cases} V^{-1/2} \exp(i(\vec{k} + \vec{K}_n)\vec{R}), & \vec{R} \in I \\ \sum_{l,m} \mathcal{R}_{l,m}^{n,\alpha}(r, E_l) Y_{l,m}(\hat{r}), & \vec{R} \in MT(\alpha) \end{cases} \quad (1)$$

with radial parts

$$\mathcal{R}_{l,m}^{n,\alpha}(r, E_l) = A_{l,m}^{n,\alpha} u_l(r, E_l) + B_{l,m}^{n,\alpha} \dot{u}_l(r, E_l). \quad (2)$$

Here the index α refers to the type of atom (or MT -sphere) in the unit cell, the radius r is counted from the center \vec{R}_α of the sphere α (i.e. $\vec{r} = \vec{R} - \vec{R}_\alpha$), V is the volume of the unit cell. Radial functions $u_{l,m}(r, E_l)$ are solutions of the Schrödinger equation in the spherically averaged crystal potential computed at the linearization energy E_l , and $\dot{u}_l(r, E_l)$ is the derivative of $u_{l,m}$ with respect to E at E_l . The coefficients $A_{l,m}^n$ and $B_{l,m}^n$ are found from the condition that the basis function ϕ_n is continuous with continuous derivative at the sphere boundary, $r = R_{MT}^\alpha$ (R_{MT}^α is the radius of the MT -sphere α). In the following for compactness we omit the index α and restore it when needed. Linearization

energies E_l are chosen close to average values of corresponding band energies or to the Fermi level. The extended electron basis states defined by Eq. (1) as a rule are orthogonal to the core states. This is a consequence of the relation

$$\int_0^{R_{MT}} \mathcal{U}_v(r) \mathcal{U}_c(r) r^2 dr = \frac{R_{MT}^2}{2(E_c - E_v)} \times \left(\mathcal{U}_c(R_{MT}) \frac{\partial \mathcal{U}_v(R_{MT})}{\partial r} - \mathcal{U}_v(R_{MT}) \frac{\partial \mathcal{U}_c(R_{MT})}{\partial r} \right), \quad (3)$$

applied to a core state with orbital quantum numbers l, m and the radial wave function $\mathcal{U}_c(r)$, and a partial radial function of valence state, $\mathcal{U}_v(r) = \mathcal{R}_{l,m}^{n,\alpha}(r, E_l)$, Eq. (2), with the same angular dependence. Notice that Eq. (3) ensures the orthogonality between the extended and core states if two conditions at the sphere boundary are satisfied for each of the core states,

$$\mathcal{U}_c(R_{MT}) = 0, \quad (4a)$$

$$\frac{\partial \mathcal{U}_c(R_{MT})}{\partial r} = 0. \quad (4b)$$

Although these conditions are met for a great number of cases, they are violated for so called semicore states that are not fully contained in the muffin-tin sphere [7–9].

Semicore states leaking out of the MT -regions should be treated as extended states. This in turn requires that the linearization energy E_l is chosen near the energy of the semicore level, $E_l \approx E_c$, because the LAPW basis describes only states near E_l well. However, as E_c is quite far from the Fermi energy E_F and the valence band energy, the choice $E_l \approx E_c$ inevitably gives poor description for partial $l = l_c$ valence states. On the other hand, the option $E_l = E_v$ is not satisfactory for the semicore states situated substantially deeper in energy. As discussed in Refs. [7, 9, 11–14] there is no simple solution to this dilemma. Even worse, in many cases the attempt to use a single value of E_l for both valence and semicore states leads to the appearance of so called “ghost bands” [7, 9] giving false band energy positions. As a remedy one can divide the energy spectrum in two windows (energy panels) and use two different sets of E_l for calculations of semicore and valence states, respectively [5]. This technique however is also not fully satisfactory because now there is no single Hamiltonian matrix for the problem and strict orthogonality between electron states belonging to different energy windows is not guaranteed. Ideally, in the MT -region there should be two different types of radial components with the same angular dependence $l = l_c$. That is, in Eq. (1)

$$\mathcal{R}_{l,m}^n(r) = \mathcal{R}_{l,m}^{(1),n}(r) + \mathcal{R}_{l,m}^{(2),n}(r), \quad (5a)$$

where

$$\mathcal{R}_{l,m}^{(1),n}(r, E_l^{(1)}) = A_{l,m}^{(1),n} u_l^{(1)}(r, E_l^{(1)}) + B_{l,m}^{(1),n} \dot{u}_l^{(1)}(r, E_l^{(1)}) \quad (5b)$$

refers to the semicore states with $E_l^{(1)} = E_c$, and

$$\mathcal{R}_{l,m}^{(2),n}(r, E_l^{(2)}) = A_{l,m}^{(2),n} u_l^{(2)}(r, E_l^{(2)}) + B_{l,m}^{(2),n} \dot{u}_l^{(2)}(r, E_l^{(2)}) \quad (5c)$$

refers to the valence states with $E_l^{(2)} = E_v \approx E_F$. Both states, Eqs. (5b) and (5c), should merge to a single l_c -wave component of the plane wave

$$\phi_n(\vec{k}, \vec{R}) = V^{-1/2} \exp(i(\vec{k} + \vec{K}_n)\vec{R}) \quad (5d)$$

at the surface of MT sphere. Now, however the boundary problem becomes ill-defined, because for the $l = l_c$ component there are four coefficients, $A_{l,m}^{(1),n}$, $B_{l,m}^{(1),n}$, $A_{l,m}^{(2),n}$ and $B_{l,m}^{(2),n}$ for only two boundary conditions.

In Ref. [7] Singh has proposed to increase the number of boundary conditions to four by matching the value of the basis function and its first three radial derivatives at the sphere surface. This gives rise to super-linearized APW method denoted as SLAPW-4 [7] because four functions, four coefficients and four boundary conditions are involved. In a simpler super-linearized modification called SLAPW-3 [7] the first radial part $\mathcal{R}_{l,m}^{(1),n}$, Eq. (5b), is supplemented by only one function $u_l^{(2)}$ (instead of $\mathcal{R}_{l,m}^{(2),n}$, Eq. (5c)). The three coefficients ($A_{l,m}^{(1),n}$, $B_{l,m}^{(1),n}$, $A_{l,m}^{(2),n}$) are determined by requiring continuity of the basis function and its two derivatives.

In comparison with standard LAPW method in both SLAPW modifications there are additional requirements for the plane wave convergence. Indeed, the plane wave expansion of the interstitial region must converge either to the correct second and third derivative (SLAPW-4) or to the second derivative (SLAPW-3). Because of that more plane waves are needed to satisfy these additional requirements, the plane wave energy cutoff parameter should be increased and calculations become much more costly [7],[5].

To circumvent the problem and improve the LAPW efficiency Singh put forward a third approach based on local orbitals (LAPW+LO) [7]. In the LAPW+LO approach the same three radial functions as in SLAPW-3 are used (i.e. $u_l^{(1)}$, $\dot{u}_l^{(1)}$ and $u_l^{(2)}$), but the coefficient of $u_l^{(2)}$ is fixed (say, $A_{l,m}^{(2),n} = 1$) and the two remaining coefficients ($A_{l,m}^{(1),n}$, $B_{l,m}^{(1),n}$) are found from the conditions that the local orbital goes to zero with zero derivative at the sphere boundary. Nowadays, LAPW+LO is widely used for band structure calculations of solids with semicore states [5, 6]. However, conceptually the LAPW+LO method is understood as a procedure giving additional variational freedom through an increase of the number of basis functions. It is not clear why additional basis functions should include these particular components (i.e. $u_l^{(1)}$, $\dot{u}_l^{(1)}$ and $u_l^{(2)}$). The proposed zero boundary conditions for local functions are not derived from a general physical statement.

Inspired by the LAPW+LO method [7] in the present study we formulate a more general approach to the prob-

lem. Unlike the LAPW+LO approach which uses variational arguments for its foundation, we will derive supplemented basis states from the initial requirement that two different radial functions (i.e. $\mathcal{R}_{l,m}^{(1),n}$ and $\mathcal{R}_{l,m}^{(2),n}$, Eqs. (5b), (5c)), having the same angular part merge in a single plane wave function ϕ_n , Eq. (5d), in the interstitial region. Unlike SLAPW-4 or SLAPW-3 we retain only two joining conditions across the MT -sphere boundary. As a result, we will obtain two types of supplementary tight-binding basis functions (see Eqs. (15b) and (15c) below), satisfying Bloch's theorem.

III. DESCRIPTION OF THE METHOD

As discussed in Sec. II, in the case of semicore states we have two types of radial solutions in the MT-region with the same angular dependence $Y_{l,m}(\hat{r})$ but different linearization energies $E_l^{(1)}$ and $E_l^{(2)}$: $\mathcal{R}_{l,m}^{(1),n}(r, E_l^{(1)})$, Eq. (5b), and $\mathcal{R}_{l,m}^{(2),n}(r, E_l^{(2)})$, Eq. (5c). One of the radial functions can refer to extended states, i.e. $R_e(r) = \mathcal{R}_{l,m}^{(1),n}(r, E_l^{(1)})$, while the other can refer to supplementary angular states $R_s(r) = \mathcal{R}_{l,m}^{(2),n}(r, E_l^{(2)})$. As we will see later in Sec. IV in practice we describe the semicore states as extended states with $E_l = E_{core}$ and valence states with the same l as supplementary states for which $E_l = E_v$. (For metals one can take $E_l = E_v \approx E_F$.) Since in the interstitial I -region both types of solutions are represented by the plane wave function $\phi_n(\vec{k}, \vec{R})$, Eq. (5d), they become indistinguishable there. In the LAPW method there are two matching conditions (for the function and its derivative) on the sphere boundary. Therefore, in our case we have

$$A_e u_e + B_e \dot{u}_e + A_s u_s + B_s \dot{u}_s = \frac{4\pi}{\sqrt{V}} i^l j_l(k_n R_{MT}) Y_{l,m}^*(\hat{k}_n) e^{i\vec{k}_n \vec{R}_\alpha}, \quad (6a)$$

$$A_e u'_e + B_e \dot{u}'_e + A_s u'_s + B_s \dot{u}'_s = \frac{4\pi}{\sqrt{V}} i^l j'_l(k_n R_{MT}) Y_{l,m}^*(\hat{k}_n) e^{i\vec{k}_n \vec{R}_\alpha}. \quad (6b)$$

Here we adopt short notations $A_e = A_{l,m}^{(1),n}$, $A_s = A_{l,m}^{(2),n}$, $u_e = u_l^{(1)}(R_{MT}, E_l^{(1)})$, $u_s = u_l^{(2)}(R_{MT}, E_l^{(2)})$, $u'_e = \partial u_l^{(1)}(R_{MT}, E_l^{(1)})/\partial r$, $u'_s = \partial u_l^{(2)}(R_{MT}, E_l^{(2)})/\partial r$, and have used the Rayleigh expansion of the plane wave ϕ_n on the sphere surface. Since there are four coefficients (A_e , B_e , A_s and B_s) and only two equations, it is clear that the general solution to Eqs. (6a), (6b), forms a two dimensional linear space with two linear independent basis vectors.

Further, introducing standard LAPW quantities $a_e =$

$a_l^{(1),n}$, $b_e = b_l^{(1),n}$, where

$$A_e = \frac{4\pi}{\sqrt{V}} i^l R_{MT}^2 Y_{l,m}^*(\hat{k}_n) e^{i\vec{k}_n \vec{R}_\alpha} a_e, \quad (7a)$$

$$B_e = \frac{4\pi}{\sqrt{V}} i^l R_{MT}^2 Y_{l,m}^*(\hat{k}_n) e^{i\vec{k}_n \vec{R}_\alpha} b_e. \quad (7b)$$

and analogous relations for a_s , b_s , we rewrite Eqs. (6a), (6b) as

$$a_e u_e + b_e \dot{u}_e + a_s u_s + b_s \dot{u}_s = j_l(k_n R_{MT}) \frac{1}{R_{MT}^2}, \quad (8a)$$

$$a_e u'_e + b_e \dot{u}'_e + a_s u'_s + b_s \dot{u}'_s = j'_l(k_n R_{MT}) \frac{1}{R_{MT}^2}. \quad (8b)$$

Notice that the standard LAPW solution for $a_e = a_e^0$ and $b_e = b_e^0$ without supplementary states, i.e. when $a_s = 0$, $b_s = 0$, can be found from the following system

$$a_e^0 u_e + b_e^0 \dot{u}_e = j_l(k_n R_{MT}) \frac{1}{R_{MT}^2}, \quad (9a)$$

$$a_e^0 u'_e + b_e^0 \dot{u}'_e = j'_l(k_n R_{MT}) \frac{1}{R_{MT}^2}. \quad (9b)$$

Defining auxiliary quantities t_a and t_b

$$t_a = a_e - a_e^0, \quad (10a)$$

$$t_b = b_e - b_e^0. \quad (10b)$$

and subtracting Eq. (9a) from Eq. (8a), and Eq. (9b) from Eq. (8b) we arrive at

$$t_a u_e + t_b \dot{u}_e + a_s u_s + b_s \dot{u}_s = 0, \quad (11a)$$

$$t_a u'_e + t_b \dot{u}'_e + a_s u'_s + b_s \dot{u}'_s = 0. \quad (11b)$$

The solution to Eqs. (11a), (11b) can be found from the following two systems,

$$\begin{cases} a_{s,1} u_s + b_{s,1} \dot{u}_s = -u_e \\ a_{s,1} u'_s + b_{s,1} \dot{u}'_s = -u'_e \end{cases}, \quad (12a)$$

$$\begin{cases} a_{s,2} u_s + b_{s,2} \dot{u}_s = -\dot{u}_e \\ a_{s,2} u'_s + b_{s,2} \dot{u}'_s = -\dot{u}'_e \end{cases}. \quad (12b)$$

Solutions to the systems (12a) and (12b) are quoted explicitly in Appendix A, Eqs. (A1a)-(A2b). Having found $a_{s,i}$ and $b_{s,i}$ ($i = 1, 2$), we write the general solution to Eqs. (8a), (8b) as

$$a_e = a_e^0 + t_a, \quad (13a)$$

$$b_e = b_e^0 + t_b, \quad (13b)$$

$$a_s = t_a a_{s,1} + t_b a_{s,2}, \quad (13c)$$

$$b_s = t_a b_{s,1} + t_b b_{s,2}, \quad (13d)$$

where t_a and t_b are arbitrary numbers. The full radial component $\mathcal{R}_{l,m}^n(r)$ of the basis function inside the MT -sphere α , Eq. (5a), is written as

$$\mathcal{R}_{l,m}^n(r) \sim a_e^0 u_e + b_e^0 \dot{u}_e + t_a (u_e + a_{s,1} u_s + b_{s,1} \dot{u}_s) + t_b (\dot{u}_e + a_{s,2} u_s + b_{s,2} \dot{u}_s). \quad (14)$$

(Here notations $u_e = u_e(r)$, $u_s = u_s(r)$ etc. refer to radial functions.)

Notice that since the coefficients t_a and t_b are arbitrary, they should be found from the standard variational procedure by requiring the minimization of the LAPW ground state energy. Furthermore, the form (14) suggests considering three linear independent radial parts (i.e. $R_{l,m}^e(r)$, $R_{l,m}^{s,1}(r)$, $R_{l,m}^{s,2}(r)$) instead of the single function $\mathcal{R}_{l,m}^n(r) = R_{l,m}^e(r) + t_a R_{l,m}^{s,1}(r) + t_b R_{l,m}^{s,2}(r)$. Explicitly,

$$R_{l,m}^e(r) = C_n e^{i\vec{k}_n \vec{R}_\alpha} (a_e^0 u_e + b_e^0 \dot{u}_e), \quad (15a)$$

$$R_{l,m}^{s,1}(r) = C_n e^{i\vec{k}_n \vec{R}_\alpha} (u_e + a_{s,1} u_s + b_{s,1} \dot{u}_s), \quad (15b)$$

$$R_{l,m}^{s,2}(r) = C_n e^{i\vec{k}_n \vec{R}_\alpha} (\dot{u}_e + a_{s,2} u_s + b_{s,2} \dot{u}_s). \quad (15c)$$

Here $u_e = u_e(r)$, $u_s = u_s(r)$ etc. are corresponding radial functions and

$$C_n = \frac{4\pi}{\sqrt{V}} i^l R_{MT}^2 Y_{l,m}^*(\hat{k}_n). \quad (16)$$

The first function, Eq. (15a), is in fact the standard radial part of the l -type, $R_{l,m}^e = \mathcal{R}_{l,m}^{n,\alpha}$, Eq. (2), entering the usual LAPW basis function $\phi_n(\vec{k}, \vec{R})$, Eq. (1). Its coefficients a_e^0 and b_e^0 are given by the LAPW boundary relations, Eqs. (9a), (9b). Two other functions however are very different from $\phi_n(\vec{k}, \vec{R})$ and should be included to the LAPW basis set as extra basis states,

$$\phi_{s,i}(\vec{k}, \vec{R}) = Y_l^m(\hat{r}) R_{l,m}^{s,i}(r), \quad (17)$$

where $i = 1, 2$. The important thing is that their coefficients $a_{s,1}$, $b_{s,1}$ are found from Eq. (12a), while coefficients $a_{s,2}$, $b_{s,2}$ from Eq. (12b). In respect to two new functions $R_{l,m}^{s,i}$, Eqs. (12a), (12b) impose the following boundary conditions

$$R_{l,m}^{s,i}(r) = 0, \quad (18a)$$

$$\frac{\partial R_{l,m}^{s,i}(r)}{\partial r} = 0. \quad (18b)$$

These relations have a simple interpretation: new supplementary basis functions $\phi_{s,i}(\vec{k}, \vec{R})$ are required to be orthogonal to the standard LAPW radial functions. We want to stress here, that the conditions (18a) and (18b) are not assumed or introduced at our will. They are derived from the initial equations (6a), (6b) [or equivalently from Eqs. (8a), (8b)] and are used to obtain the general solution, Eqs. (13a)-(13d).

From Eq. (15b), (15c) and (16) it follows that the supplementary basis states in principle depend on the index n , i.e. $\phi_{s,i}(\vec{k}, \vec{R}) = \phi_{s,i}(\vec{k}_n, \vec{R})$. (We recall that $\vec{k}_n = \vec{k} + \vec{K}_n$, where \vec{K}_n is a vector of the reciprocal lattice.) However, since all functions $\phi_{s,i}(\vec{k}_n, \vec{R})$ with different index n have the same radial part, $\mathcal{U}^{s,1}(r) = u_e + a_{s,1} u_s + b_{s,1} \dot{u}_s$ for $i = 1$, or $\mathcal{U}^{s,2}(r) = \dot{u}_e + a_{s,2} u_s + b_{s,2} \dot{u}_s$

for $i = 2$, they are simply proportional to each other, $\phi_{s,i}(\vec{k}_n, \vec{R}) \sim \phi_{s,i}(\vec{k}_{n'}, \vec{R})$. Therefore, to avoid the linear dependence we should choose only one set of functions $\phi_{s,i}(\vec{k}_n, \vec{R})$ corresponding to a single index n . The obvious choice is to use the function $\phi_{s,i}(\vec{k}, \vec{R})$ with $n = 0$, $\vec{k}_0 = \vec{k}$ and the reciprocal lattice vector $\vec{K}_0 = 0$. In that case the coefficient $C_0 = \pi/V i^l R_{MT}^2 Y_{l,m}^*(\hat{k})$ [compare with Eq. (16)] can be further rationalized by omitting the multiplier $Y_{l,m}^*(\hat{k})$ [or equivalently, including it in factors t_a and t_b , Eq. (10a), (10b)]. Thus, we substitute C_0 with

$$C_0 = \frac{4\pi}{\sqrt{V}} i^l R_{MT}^2. \quad (19)$$

(In principle, since the local function is not orthonormal, we can simply put $C_0 = 1$, but the form (19) being similar to the constant coefficient for the standard LAPW basis function, simplifies some expressions for programming.)

To study the transformational properties of supplementary basis functions $\phi_{s,i}(\vec{k}, \vec{R})$, Eq. (17), we first rewrite them in the following form,

$$\phi_{s,i}(\vec{k}, \vec{R}) = e^{i\vec{k}\vec{R}_\alpha} \psi_i^{l,m}(\vec{R} - \vec{R}_\alpha), \quad (20)$$

where for each site α we have introduced two local functions ($i = 1, 2$) of the l, m -type,

$$\psi_i^{l,m}(\vec{R} - \vec{R}_\alpha) = C_0 \mathcal{U}^{s,i}(r) Y_l^m(\hat{r}). \quad (21)$$

Notice that each local function $\psi_i^{l,m}(\vec{R} - \vec{R}_\alpha)$ is strictly confined inside the MT -sphere α , because both $\mathcal{U}^{s,i}(r)$ and $R_l^{s,i}(r)$ satisfy the boundary conditions (18a), (18b). We can then extend the function $\phi_{s,i}(\vec{k}, \vec{R})$ to the interstitial region ($\vec{R} \in I$) by requiring $\phi_{s,i}(\vec{k}, \vec{R}) = 0$. For the whole crystal we thus have

$$\begin{aligned} \phi_{s,i}(\vec{k}, \vec{R}) &= \sum_{\alpha} e^{i\vec{k}\vec{R}_\alpha} \psi_i^{l,m}(\vec{R} - \vec{R}_\alpha), & \vec{R} \in MT, \\ \phi_{s,i}(\vec{k}, \vec{R}) &= 0, & \vec{R} \in I. \end{aligned} \quad (22)$$

This is a clear manifestation of the tight binding wave function. The multiplier $e^{i\vec{k}\vec{R}_\alpha}$ in Eqs. (22) and (20) ensures that the supplementary wave functions $\phi_{s,i}(\vec{k}, \vec{R})$ obey the Bloch theorem. It is worth noting that usually the tight-binding description is spoiled by the presence of overlap between tails of wave function centered at neighboring sites. In the present method the tight-binding functions, Eqs. (22) and (20), are free from this disadvantage because the local functions (and their first derivatives) go to zero at the sphere boundary and the overlap is absent. Thus, supplementary tight-binding functions can be considered as additional basis states orthogonal to the standard LAPW basis set.

All matrix elements between the supplementary basis functions $\phi_{s,i}$ in the spherically symmetric potential are quoted explicitly in Appendix B, and all matrix elements between $\phi_{s,i}$ and standard LAPW basis functions ϕ_n are listed in Appendix C. For brevity we do not quote here

the partial charges and electron density associated with supplementary basis states. They are tightly connected with the overlap matrix elements given by Eqs. (B2a), (B4a) and (B5a) of Appendix B, and Eqs. (C2a), (C3a) of Appendix C. Concerning the full potential expressions for the extended basis set it is worth noting that after some algebraic transformations the equations can be obtained by selecting in standard FLAPW equations the contributions with the orbital indices l, m referring to the components of supplemented states and combining them together according to Eqs. (15b), (15c), (17).

The tight binding basis functions have a very important and practical property: they work even in the case when their expansion energy E_s lies not far from the LAPW linear expansion energy E_e . (We recall that the whole procedure is designed to treat the complicated case of semicore states when E_s is supposed to be separated from E_e by at least 10 eV.) The limiting case $E_s \approx E_e$ is considered in detail in Appendix D, and also discussed in calculations of Cd in Sec. IV C.

IV. PRACTICAL IMPLEMENTATION

A. Face centered cubic structure of La

We have applied the method developed in Sec. III to full potential electron band structure calculations of face centered cubic (fcc) structure of lanthanum. Atomic lanthanum has completely filled $5p$ semicore electron shell lying at -22.12 eV which can slightly mix with valence states ($5d$, $6s$, $4f$) at energies from -3 to -2 eV. For lanthanum here and below we use the Perdew-Burke-Ernzerhof (PBE) [15] variant of the generalized gradient approximation (GGA) which gives rather accurate lattice constants for our systems.

We have employed our original version of LAPW code with the potential of general form [16]. Integration in the irreducible part of the Brillouin zone has been performed over 240 special points. Angular expansions for the electron density and wave function inside MT -sphere have been done up to $L_{max} = 8$. The number of basis functions has been limited by the condition $K_{max} R_{MT} = 9.0$, resulting in 65 basis states. In addition to the standard LAPW basis functions we have considered 6 supplementary tight binding basis functions with the p -angular dependence, which are located strictly inside the MT -sphere, Sec. III.

The $5p$ semicore states have been treated as band states with the LAPW linear expansion energy E_e lying 0.5 eV above the p -band bottom energy (which is -9.5 eV for the equilibrium lattice constant $a = 5.315$ Å). The linear expansion energy for supplementary tight binding p -states has been fixed at 1 eV below the Fermi energy, $E_s(p) = 6.10$ eV. Under these conditions two supplementary radial functions shown in Fig. 1 are given by

$$R_1(r) = u_e(r) + a_{s,1}u_s(r) + b_{s,1}\dot{u}_s(r), \quad (23a)$$

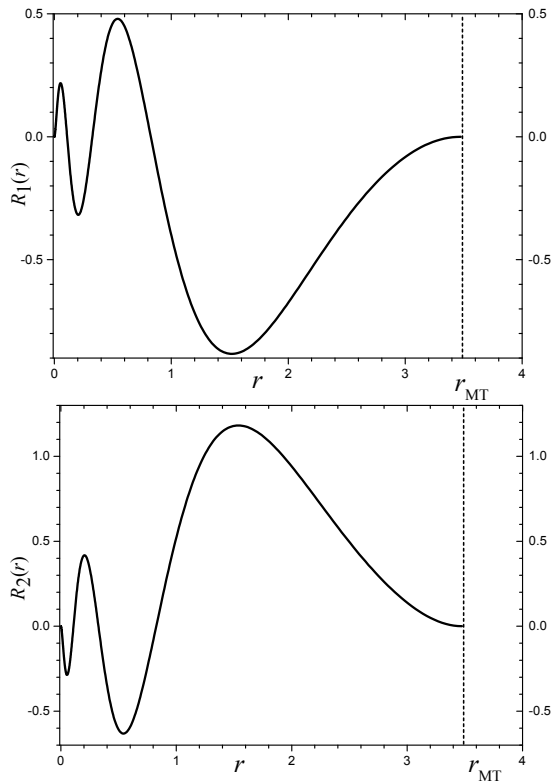


FIG. 1: Two supplemented tight binding radial functions of p -type for face centered cubic (fcc) structure of lanthanum ($a = 5.315$ Å). Radius is given in Å, $r_{MT} = 3.474$ Å stands for the muffin-tin radius.

where $a_{s,1} = 0.1940$, $b_{s,1} = 0.4041$, and

$$R_2(r) = \dot{u}_e(r) + a_{s,2}u_s(r) + b_{s,2}\dot{u}_s(r), \quad (23b)$$

where $a_{s,2} = -1.9609$, $b_{s,2} = 1.0705$. Notice that the number of nodes for both radial functions is three (excluding points with $r = 0$ and $r = r_{MT}$) which allows us to consider these functions as “compressed” $5p$ basis states (i.e. with the principal quantum number $n = 5$) strictly confined within MT-sphere. The iteration procedure with supplemented tight binding functions has been stable converging to a self consistent solution without additional difficulties. Our PBE-GGA calculations result in equilibrium fcc lattice constant $a = 5.315$ Å which compares well with the experimental value, $a_{exp} = 5.304$ Å, Ref. 17.

To compare our treatment with the standard (LAPW+LO) method which uses only the first local function $R_1(r)$, Eq. (23a), we have performed a series of calculations, the results of which are summarized in Tables I, II, III. In all cases the present method gives lower values of the total energy, Table I. However, the energy difference which amounts to 0.145 eV for the poor basis set ($K_{max}R_{MT} = 7$) becomes smaller for the intermediate basis sets and decreases to a small value (0.004 eV) for the best basis set ($K_{max}R_{MT} = 9$). Nevertheless, even this difference is clearly noticeable in energy

TABLE I: Total energy (E_{tot} , in eV) for various basis sets for fcc calculations of La. $a = 5.315$ Å, $R_{MT} = 3.474$ Å, $E_0 = -231170$ eV, $\Delta E = E_{tot}(\text{FLAPW++}) - E_{tot}(\text{FLAPW+})$. FLAPW++ stands for the present scheme (FLAPW + 2STBFs) with two radial functions and FLAPW+ for the FLAPW + LO method with a single radial function.

$R_{MT} \cdot K_{max}$	FLAPW++	FLAPW+	ΔE
7.0	$E_0 - 8.6878$	$E_0 - 8.5432$	-0.1446
7.5	$E_0 - 9.2282$	$E_0 - 9.1730$	-0.0552
8.0	$E_0 - 9.5362$	$E_0 - 9.5301$	-0.0061
9.0	$E_0 - 9.5635$	$E_0 - 9.5599$	-0.0036

TABLE II: Energy parameters (in eV) for various basis sets for fcc calculations of La ($a = 5.315$ Å, $R_{MT} = 3.474$ Å). FLAPW++ stands for the present scheme (FLAPW + 2STBFs) with two radial functions and FLAPW+ for the FLAPW + LO method with a single radial function.

	$R_{MT} K_{max}$	semicore 5 <i>p</i> -band		valence (<i>spd</i>)-band	
		E_{bot}	E_{top}	E_{bot}	E_F
FLAPW++	7.0	-11.1905	-9.9254	2.7704	6.2047
	7.5	-10.9033	-9.5956	2.9965	6.3020
	8.0	-10.0729	-8.7075	3.7651	7.0381
	9.0	-9.9972	-8.6297	3.8310	7.1009
FLAPW+	7.0	-10.9433	-9.6852	2.9275	6.3934
	7.5	-10.7326	-9.4289	3.1170	6.4386
	8.0	-9.9564	-8.5890	3.8695	7.1478
	9.0	-9.9240	-8.5550	3.8958	7.1695

band characteristics. In particular, band energy spectrum demonstrates that the energy difference is of ≈ 0.07 eV for the best basis set, Tables II, III. It is worth noting that for all basis sets the present method results gives smaller band energies, Table II.

TABLE III: Energy band spectrum (in eV) of fcc La ($a = 5.315$ Å, $R_{MT} = 3.474$ Å, $R_{MT} \cdot K_{max} = 9$) at the Γ -point of the Brillouin zone. FLAPW++ stands for the present scheme (FLAPW + 2STBFs) with two radial functions and FLAPW+ for the FLAPW + LO method with a single radial function.

band	deg.	FLAPW++	FLAPW+
1	(3)	-8.6297	-8.5550
2		3.8310	3.8958
E_F		7.1009	7.1695
3		8.5444	8.6258
5	(3)	8.6128	8.6803

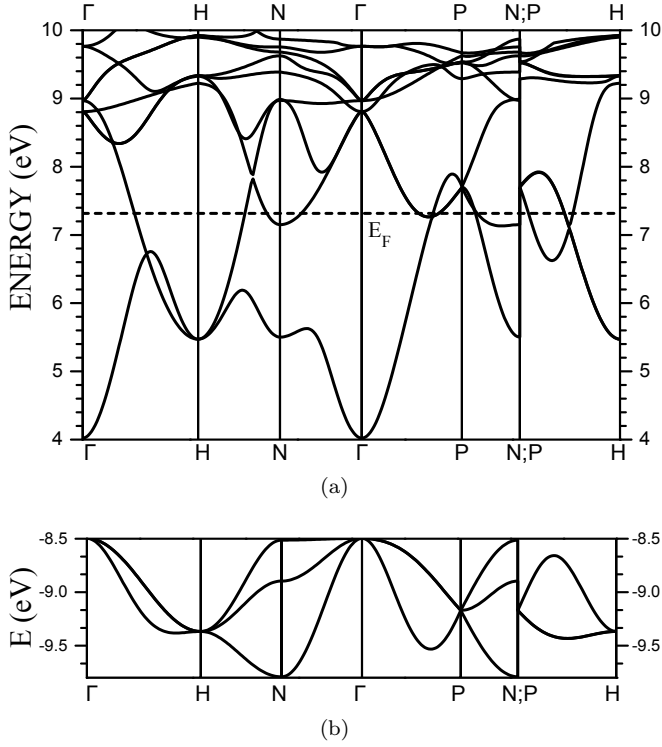


FIG. 2: Electronic band structure of bcc γ -La along high symmetry lines of the Brillouin zone ($a = 4.243$ Å). (a) valence bands, (b) semicore (5p) band. The horizontal dashed line indicates the Fermi level.

B. Body centered cubic structure of La

For the body centered cubic (bcc) phase of lanthanum we have used a plane wave cut off parameter $K_{max}R_{MT} = 9$ (79 basis states plus 6 additional tight binding p -states), $L_{max} = 8$ for the expansion of the electron density and wave functions inside MT-spheres, 285 special points in the irreducible part of the Brillouin zone during the self-consistent procedure.

As for fcc-La the LAPW linear expansion energy for the extended p -states of bcc-La has been chosen at 0.5 eV above the p -band bottom energy (i.e. $E_e(p) = -9.29$ eV for the equilibrium lattice constant $a = 4.243$ Å). The linear expansion energy for the supplemented tight binding p -states has been fixed at 1.0 eV below the Fermi energy ($E_s(p) = 6.32$ eV). Two supplemented radial functions, quoted in Eqs. (23a) and (23b), are defined by the coefficients $a_{s,1} = 0.1502$, $b_{s,1} = 0.4844$ for $R_1(r)$, and $a_{s,2} = -1.8251$, $b_{s,2} = 0.7718$ for $R_2(r)$.

The equilibrium lattice constant found for bcc-La, $a = 4.243$ Å, is in good correspondence with the experimental value $a_{exp} = 4.25$ Å [18]. The calculated band structure of bcc lattice of lanthanum (PBE exchange and correlation) is plotted in Fig. 2.

The results of the present and LAPW+LO approaches are compared in Tables IV, V and VI. As for fcc-La, the present scheme gives lower values of total energy of

TABLE IV: Total energy (E_{tot} , in eV) for various basis sets for bcc calculations of La. $a = 4.243$ Å, $R_{MT} = 3.355$ Å, $E_0 = -231170$ eV, $\Delta E = E_{tot}(\text{FLAPW++}) - E_{tot}(\text{FLAPW+})$. FLAPW++ stands for the present scheme (FLAPW + 2STBFs) with two radial functions and FLAPW+ for the FLAPW + LO method with a single radial function.

$R_{MT} \cdot K_{max}$	FLAPW++	FLAPW+	ΔE
7.0	$E_0 - 8.8166$	$E_0 - 8.7373$	-0.0793
8.0	$E_0 - 9.3567$	$E_0 - 9.3428$	-0.0139
9.0	$E_0 - 9.4574$	$E_0 - 9.4545$	-0.0029

TABLE V: Energy parameters (in eV) for various basis sets for bcc calculations of La ($a = 4.243$ Å, $R_{MT} = 3.355$ Å). FLAPW++ stands for the present scheme (FLAPW + 2STBFs) with two radial functions and FLAPW+ for the FLAPW + LO method with a single radial function.

$R_{MT} K_{max}$	semicore 5p-band		valence (spd)-band	
	E_{bot}	E_{top}	E_{bot}	E_F
FLAPW++	7.0	-10.7891 -9.5738	3.1271	6.5415
	8.0	-10.2179 -8.9376	3.6086	6.9193
	9.0	-9.7907 -8.4968	4.0213	7.3193
FLAPW+	7.0	-10.5792 -9.3654	3.2761	6.7062
	8.0	-10.0659 -8.7832	3.7403	7.0573
	9.0	-9.7178 -8.4227	4.0875	7.3877

bcc-La for all basis sets. The total energy difference increases with worsening of the basis quality, Table IV. For the best basis set ($R_{MT} \cdot K_{max} = 9$) the present method gives energy spectrum shifted downwards by ≈ 0.07 eV in comparison with FLAPW+LO band energy values, Tables VI, V. The difference between energy bands parameters reaches 0.2 eV for poor basis set ($R_{MT} \cdot K_{max} = 7$), Table V. For the best basis set the total energy of bcc-La (γ -phase) is ~ 0.1 eV higher than the total energy of fcc-La (β -phase), Tables I and IV, which is in agreement with the fact that at normal pressure γ -La exists only

TABLE VI: Energy band spectrum (in eV) of bcc La ($a = 4.243$ Å, $R_{MT} = 3.355$ Å, $R_{MT} \cdot K_{max} = 9$) at the Γ -point of the Brillouin zone. FLAPW++ stands for the present scheme (FLAPW + 2STBFs) with two radial functions and FLAPW+ for the FLAPW + LO method with a single radial function.

band	deg.	FLAPW++	FLAPW+
1	(3)	-8.4968	-8.4227
2		4.0213	4.0875
E_F		7.3193	7.3877
3	(3)	8.8077	8.8758
5	(3)	8.9685	9.0497

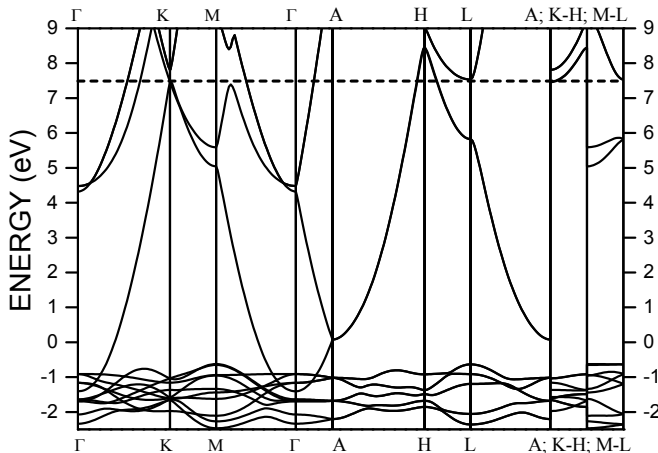


FIG. 3: (a) Electronic band structure of hexagonal close packed Cd along high symmetry lines of the Brillouin zone ($a = 2.986 \text{ \AA}$, $c = 5.632 \text{ \AA}$).

at high temperatures ($>1138 \text{ K}$) in narrow temperature range (53 K) [18].

C. Hexagonal close packed structure of Cd

Hexagonal close packed (hcp) cadmium is a special case because its $4d$ -states are not separated from the valence $5s$ -states by an energy gap, Fig. 3. In fact there is a small overlap between the top of d -band and the bottom of s -band. This implies that if the linear expansion energy of extended d -states is properly chosen (for example, at 0.5 eV above the d -band bottom energy, $E(d) = -1.97 \text{ eV}$) the electronic band structure of cadmium can be carried out without supplemented tight-binding basis states of d -type. Thus, both calculations i.e. with and without supplemented states, can be directly compared with each other. The second peculiarity is that because of the gapless energy spectrum the radial distribution of d -states does not change much throughout the valence band. If we chose the linear expansion energy of supplemented d -states at 1.0 eV below the Fermi energy ($E_s(d) = 6.42 \text{ eV}$), then the energy difference $E_s(d) - E_e(d) \sim 8.5 \text{ eV}$ is a relatively small value. In that case one can expect that the extended d -states and the supplemented d -states are close to being linearly dependent, and we can test the scenario described in Appendix D. (Two supplementary radial functions, Eqs. (23a) and (23b), are specified by the coefficients $a_{s,1} = -0.3448$, $b_{s,1} = 0.4643$ for $R_1(r)$ and $a_{s,2} = -1.9343$, $b_{s,2} = -0.2952$ for $R_2(r)$.)

The technical parameters of FLAPW calculations were the following: the plane wave cut off parameter $K_{max}R_{MT} < 9$ (149 basis states and 10 supplemented tight binding d -states), $L_{max} = 8$ for the expansion of electron density and wave functions inside the MT-spheres, 216 special points in the irreducible part of the Brillouin zone during the self-consistent procedure, and

TABLE VII: Total energy (E_{tot} , in eV) for various basis sets for hcp calculations of Cd. $a = 2.986 \text{ \AA}$, $c = 5.632 \text{ \AA}$, $R_{MT} = 2.74 \text{ \AA}$, $E_0 = -304510 \text{ eV}$, $\Delta E = E_{tot}(\text{FLAPW++}) - E_{tot}(\text{FLAPW+})$. FLAPW++ stands for the present scheme (FLAPW + 2STBFs) with two radial functions and FLAPW+ for the FLAPW + LO method with a single radial function.

$R_{MT}K_{max}$	FLAPW++	FLAPW+	ΔE	FLAPW
7.0	$E_0 - 4.3780$	$E_0 - 3.8336$	-0.5444	$E_0 - 2.4724$
7.5	$E_0 - 6.6012$	$E_0 - 6.4998$	-0.1014	$E_0 - 6.3540$
8.0	$E_0 - 7.4471$	$E_0 - 7.4128$	-0.0343	$E_0 - 7.3592$
8.5	$E_0 - 7.9324$	$E_0 - 7.9033$	-0.0291	$E_0 - 7.8428$
9.0	$E_0 - 8.0093$	$E_0 - 7.9899$	-0.0194	$E_0 - 7.9459$

TABLE VIII: Energy parameters (in eV) for various basis sets for hcp calculations of Cd. FLAPW++ stands for the present scheme (FLAPW + 2STBFs) with two radial functions and FLAPW+ for the FLAPW + LO method with a single radial function.

	$R_{MT} \cdot K_{max}$	E_{bot}	E_F
FLAPW++	7.0	-3.1660	6.8094
	7.5	-2.9380	7.1192
	8.0	-2.7794	7.2053
	8.5	-2.5564	7.3358
	9.0	-2.4655	7.4186
FLAPW+	7.0	-2.9447	6.9453
	7.5	-2.8216	7.2016
	8.0	-2.6999	7.2648
	8.5	-2.4763	7.3969
	9.0	-2.3949	7.4741
FLAPW	7.0	-3.3958	7.0200
	7.5	-2.9187	7.2652
	8.0	-2.7556	7.2997
	8.5	-2.5211	7.4394
	9.0	-2.4273	7.5123

the PBE [15] form of the exchange correlation potential.

The equilibrium lattice constants are $a = 2.986 \text{ \AA}$, $c = 5.632 \text{ \AA}$, which are in good correspondence with the experimental values, $a_{exp} = 2.9794 \text{ \AA}$ and $c_{exp} = 5.6186 \text{ \AA}$ [19]. Band energies are shown in Fig. 3.

Comparison between the present approach, the LAPW+LO and the standard LAPW treatment is presented in Tables VII, VIII and IX. We observe that for all basis sets the present approach gives lower total energy values, Table VII. For the best basis set ($R_{MT}K_{max} = 9$) the obtained total energy difference with the LAPW+LO value, 0.02 eV, is larger than for fcc-La or bcc-La. In the present approach band energies computed with the best basis set are lowered by 0.04-0.09 eV in comparison with LAPW+LO and LAPW values, Tables VIII and IX. These energy shifts are also typical for the other points

TABLE IX: Energy band spectrum (in eV) of hcp structure of Cd at the Γ -point of the Brillouin zone ($a = 2.986$ Å, $c = 5.632$ Å) with PBE exchange [15] (E_F is the Fermi energy, deg. is the energy degeneracy). FLAPW++ stands for the present scheme (FLAPW + 2STBFs) with two radial functions and FLAPW+ for the FLAPW + LO method with a single radial function.

	deg.	FLAPW++	FLAPW+	FLAPW
1		-2.3356	-2.2662	-2.2954
2		-2.0708	-2.0009	-2.0305
3	(2)	-1.6919	-1.6194	-1.6604
4	(2)	-1.6399	-1.5668	-1.6078
5		-1.4047	-1.3485	-1.3215
6	(2)	-1.1638	-1.0888	-1.1334
7	(2)	-0.9125	-0.8377	-0.8866
8		4.3215	4.3750	4.4176
9		4.4792	4.5374	4.5479
E_F		7.4186	7.4741	7.5123
10		17.6841	17.7375	17.7711

of the Brillouin zone.

V. CONCLUSIONS

We have presented a new method for the improvement of the LAPW description of the electronic band structure by using two linearization energies for the same (l, m) partial component. Starting with two LAPW radial functions, Eqs. (5b) and (5c), having the same angular dependence $Y_{l,m}(\hat{r})$ but different linearization energies ($E_l^{(1)}$ and $E_l^{(2)}$) inside MT-spheres, we have demonstrated that their augmentation to the basis plane wave can be performed by constructing additional basis functions $\phi_{s,i}$ ($i = 1, 2$) in the form of Eq. (17) [two functions, Eqs. (15b) and (15c), for each l, m -component]. The supplementary basis functions have zero values and slopes on the sphere surface, Eqs. (18a), (18b), and are linear independent of the usual LAPW basis states. The constructed basis functions are of the tight-binding type, Eq. (22), and obey Bloch's law.

In contrast to the LAPW+LO method with only one supplemented function, Eq. (15b), in our treatment for each l, m -component there are two supplemented functions [Eq. (15b) and (15c)]. The second basis function (absent in LAPW+LO) closely examined in this work, owes its appearance to the \dot{u}_l function in the canonical LAPW method. Thus, the basis sets of LAPW and LAPW+LO methods can be extended further by adding supplemented functions of the tight-binding type, Eq. (15c).

In Sec. IV, the present method with extended basis set has been applied to the study of the face centered and body centered phases of lanthanum (β -La and γ -La)

with the $5p$ -semicore shell separated by a gap of forbidden states from the valence states and to the hexagonal close packed structure of cadmium, where the semicore $4d$ -states overlap with the valence $5s$ -states. In all cases we have observed a systematic improvement in the values of total energy in comparison with the standard LAPW+LO treatment, Tables I, IV, VII. The difference with LAPW+LO total energy is only 0.003-0.004 eV for La and 0.019 eV for Cd for the best basis set ($R_{MT} \cdot K_{max} = 9$) but significantly increases in going to intermediate ($R_{MT} \cdot K_{max} = 8.5$ or 8) and poor ($R_{MT} \cdot K_{max} = 7.5$ or 7) basis sets.

Acknowledgments

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Appendix A

Solution to the system of linear equations, Eq. (12a), is given by

$$a_{s,1} = \frac{1}{\Delta} (u_e \dot{u}'_s - u'_e \dot{u}_s), \quad (\text{A1a})$$

$$b_{s,1} = \frac{1}{\Delta} (u'_e u_s - u_e u'_s), \quad (\text{A1b})$$

and the solution to the system (12b) is

$$a_{s,2} = \frac{1}{\Delta} (\dot{u}_e \dot{u}'_s - \dot{u}'_e \dot{u}_s), \quad (\text{A2a})$$

$$b_{s,2} = \frac{1}{\Delta} (\dot{u}'_e u_s - \dot{u}_e u'_s). \quad (\text{A2b})$$

Here

$$\Delta = \dot{u}_s u'_s - u_s \dot{u}'_s \approx \frac{1}{R_{MT}^2}. \quad (\text{A3})$$

Appendix B

The matrix elements for the overlap and Hamiltonian operator between supplementary states,

$$\langle \phi_{s,i} | O | \phi_{s,j} \rangle = O_{s,s}^{ij}, \quad (\text{B1a})$$

$$\langle \phi_{s,i} | H | \phi_{s,j} \rangle = H_{s,s}^{ij}, \quad (\text{B1b})$$

are partitioned in three different blocks, when $i = j = 1$ (block I), $i = j = 2$ (block II), and $i = 1, j = 2$ or $i = 2, j = 1$ (block III).

For the first block (I) we have

$$O_{s,s}^{11}(\vec{k}) = \mathcal{O}_{s,s} (1 + C_{s,s}^{11} + C_{e,s}^1), \quad (\text{B2a})$$

where N_α is the number of equivalent spheres α , while

$$\mathcal{O}_{s,s} = \frac{(4\pi)^2}{V} (R_{MT}^\alpha)^4 N_\alpha, \quad (\text{B2b})$$

$$C_{s,s}^{11} = a_{s,1}a_{s,1} + b_{s,1}b_{s,1} \mathcal{N}(\dot{u}_s, \dot{u}_s), \quad (\text{B2c})$$

$$C_{e,s}^1 = a_{s,1} \mathcal{N}(u_e, u_s) + b_{s,1} \mathcal{N}(u_e, \dot{u}_s), \quad (\text{B2d})$$

and \mathcal{N} stands for the integral over the product of two functions,

$$\mathcal{N}(u_1, u_2) = \int_0^{R_{MT}} u_1(r) u_2(r) r^2 dr. \quad (\text{B3})$$

Notice that $\mathcal{N}(u_e, u_e) = \mathcal{N}(u_s, u_s) = 1$ and $\mathcal{N}(u_e, \dot{u}_e) = \mathcal{N}(u_s, \dot{u}_s) = 0$. It is also assumed here that the constant coefficient of the supplementary function is taken in the form of Eq. (19). If another form is used, the factor $\mathcal{O}_{s,s}$, Eq. (B2b), [and $\mathcal{O}_{e,s}(\vec{k}_n)$, Eq. (C2c)] should be changed accordingly.

For the block *II* we obtain

$$C_{s,s}^{22} = \mathcal{O}_{s,s} (\mathcal{N}(\dot{u}_e, \dot{u}_e) + C_{s,s}^{22} + C_{e,s}^2), \quad (\text{B4a})$$

where

$$C_{s,s}^{22} = a_{s,2}a_{s,2} + b_{s,2}b_{s,2} \mathcal{N}(\dot{u}_s, \dot{u}_s), \quad (\text{B4b})$$

$$C_{e,s}^2 = a_{s,2} \mathcal{N}(\dot{u}_e, u_s) + b_{s,2} \mathcal{N}(\dot{u}_e, \dot{u}_s). \quad (\text{B4c})$$

Finally, for the block *III* we get

$$C_{s,s}^{12} = \mathcal{O}_{s,s} (C_{s,s}^{12} + C_{e,s}^1 + C_{e,s}^2), \quad (\text{B5a})$$

where

$$C_{s,s}^{12} = a_{s,1}a_{s,2} + b_{s,1}b_{s,2} \mathcal{N}(\dot{u}_s, \dot{u}_s), \quad (\text{B5b})$$

and $C_{e,s}^1$ is given by Eq. (B2d), while $C_{e,s}^2$ by Eq. (B4c).

For the matrix elements of the Hamiltonian $H_{s,s}^{ij}(\vec{k})$, Eq. (B1b), we also obtain three blocks. For the first block (*I*) we have

$$H_{s,s}^{11} = \mathcal{O}_{s,s} (E_e + E_s C_{s,s}^{11} + a_{s,1}b_{s,1} + (E_e + E_s) C_{e,s}^1 + b_{s,1} \mathcal{N}(u_e, u_s)). \quad (\text{B6})$$

Here E_e and E_s are energies at which the radial wave functions $u_e(r)$ and $u_s(r)$ are evaluated in the *MT*-sphere α .

For the second block (*II*) we get

$$H_{s,s}^{22} = \mathcal{O}_{s,s} (E_e \mathcal{N}(\dot{u}_e, \dot{u}_e) + E_s C_{s,s}^{22} + a_{s,2}b_{s,2} + (E_e + E_s) C_{e,s}^2 + \gamma_{e,s}^2), \quad (\text{B7a})$$

where

$$\gamma_{e,s}^2 = a_{s,2} \mathcal{N}(u_e, u_s) + b_{s,2} (\mathcal{N}(u_e, \dot{u}_s) + \mathcal{N}(\dot{u}_e, u_s)). \quad (\text{B7b})$$

For the third block (*III*) we have

$$H_{s,s}^{12} = \mathcal{O}_{s,s} (E_s (C_{s,s}^{12} + C_{e,s}^1) + a_{s,2}b_{s,1} + E_e C_{e,s}^2 + b_{s,1} \mathcal{N}(\dot{u}_e, u_s)). \quad (\text{B8})$$

Appendix C

In this section we quote the expressions for matrix elements for the overlap and Hamiltonian operator between supplementary and extended states,

$$\langle \phi_{s,i} | O | \phi_n \rangle = O_{s,e}^{i,n}(\vec{k}), \quad (\text{C1a})$$

$$\langle \phi_{s,i} | H | \phi_n \rangle = H_{s,e}^{i,n}(\vec{k}). \quad (\text{C1b})$$

The extended states here are the usual LAPW basis functions, Eq. (1), which are characterized by the wave vector $\vec{k}_n = \vec{k} + \vec{K}_n$. The supplementary functions have two components $i = 1, 2$, for each l, m -angular dependence, Eq. (15b), (15c), (17).

For the matrix of overlap we get

$$O_{s,e}^{1n}(\vec{k}) = \mathcal{O}_{e,s}(\vec{k}_n) S_{s,e}^{1n}, \quad (\text{C2a})$$

where

$$S_{s,e}^{1n} = a_e + a_{s,1}a_e \mathcal{N}(u_e, u_s) + a_{s,1}b_e \mathcal{N}(\dot{u}_e, u_s) + b_{s,1}a_e \mathcal{N}(u_e, \dot{u}_s) + b_e b_{s,1} \mathcal{N}(\dot{u}_e, \dot{u}_s), \quad (\text{C2b})$$

and the structure factor is

$$\mathcal{O}_{e,s}(\vec{k}_n) = \frac{(4\pi)^2}{V} (R_{MT}^\alpha)^4 Y_{lm}^*(\hat{k}_n) \times \sum_\nu \exp[i(\vec{k}_n - \vec{k}) \cdot \vec{r}_{\nu,\alpha}]. \quad (\text{C2c})$$

Here, $\vec{r}_{\nu,\alpha}$ stands for the coordinates of all ν centers of *MT*-spheres of the type α in the primitive unit cell. The factors $\mathcal{N}(u_1, u_2)$ in (C2b) are integrals between two functions given by Eq. (B3).

The quantities a_e and b_e in Eq. (C2b) and below are standard LAPW expansion coefficients for the component with l, m , defined by Eq. (9a) and (9b), i.e. $a_e = a_e^0$ and $b_e = b_e^0$. Since they depend on \vec{k}_n , l , and α , we can write $a_e = a_l^\alpha(\vec{k})$, $b_e = b_l^\alpha(\vec{k})$. Explicit expressions for them can be found in Ref. [4, 5].

The matrix element for the second case ($i = 2$) reads as

$$O_{s,e}^{2n}(\vec{k}) = \mathcal{O}_{e,s}(\vec{k}_n) S_{s,e}^{2n}, \quad (\text{C3a})$$

where

$$S_{s,e}^{2n} = b_e \mathcal{N}(\dot{u}_e, \dot{u}_e) + a_{s,2}a_e \mathcal{N}(u_e, u_s) + a_{s,2}b_e \mathcal{N}(\dot{u}_e, u_s) + b_{s,2}a_e \mathcal{N}(u_e, \dot{u}_s) + b_e b_{s,2} \mathcal{N}(\dot{u}_e, \dot{u}_s). \quad (\text{C3b})$$

Below we quote the matrix elements for the Hamiltonian,

$$H_{s,e}^{1n}(\vec{k}) = \mathcal{O}_{e,s}(\vec{k}_n) (E_e S_{s,e}^{1n} + b_e + a_{s,1}b_e \mathcal{N}(u_e, u_s) + b_{s,1}b_e \mathcal{N}(u_e, \dot{u}_s)), \quad (\text{C4})$$

$$H_{s,e}^{2n}(\vec{k}) = \mathcal{O}_{e,s}(\vec{k}_n) (E_e S_{s,e}^{2n} + a_{s,2}b_e \mathcal{N}(u_e, u_s) + b_{s,2}b_e \mathcal{N}(u_e, \dot{u}_s)). \quad (\text{C5})$$

Here $\mathcal{O}_{e,s}$ is given by Eq. (C2c), while $S_{s,e}^{in}$ by Eq. (C2b) for $i = 1$, and by Eq. (C3b) for $i = 2$.

Appendix D

Here we demonstrate that the two supplementary basis functions $\phi_{s,i}$ ($i = 1, 2$), Eq. (17), work even in the case when the expansion energies E_s and E_e lie not far from each other.

Consider $E_e = E_s + \varepsilon$, where $\varepsilon/E_s \ll 1$. Making use of the following expansions

$$u_e(r) = u_s(r) + \dot{u}_s(r) \varepsilon + \frac{1}{2} \ddot{u}_s(r) \varepsilon^2 + \frac{1}{6} \dddot{u}_s(r) \varepsilon^3 + O(\varepsilon^4), \quad (\text{D1a})$$

$$\dot{u}_e(r) = \dot{u}_s(r) + \ddot{u}_s(r) \varepsilon + \frac{1}{2} \dddot{u}_s(r) \varepsilon^2 + O(\varepsilon^3), \quad (\text{D1b})$$

for $u_e(r)$ and $\dot{u}_e(r)$ and substituting them in Eqs. (15b), (15c), we arrive at

$$R_{l,m}^{s,1}(r) = \frac{1}{2} \varepsilon^2 C_0 e^{i\vec{k}\vec{R}_\alpha} [\ddot{u}_s + \frac{1}{3} \varepsilon \dddot{u}_s + O(\varepsilon^2) + a'_{s,1} u_s + b'_{s,1} \dot{u}_s], \quad (\text{D2a})$$

$$R_{l,m}^{s,2}(r) = \varepsilon C_0 e^{i\vec{k}\vec{R}_\alpha} [\ddot{u}_s + \frac{1}{2} \varepsilon \dddot{u}_s + O(\varepsilon^2) + a'_{s,2} u_s + b'_{s,2} \dot{u}_s]. \quad (\text{D2b})$$

Here

$$a'_{s,1} = \frac{1}{\varepsilon^2} (a_{s,1} + 1), \quad b'_{s,1} = \frac{1}{\varepsilon^2} (b_{s,1} + \varepsilon); \quad (\text{D3a})$$

$$a'_{s,2} = \frac{1}{\varepsilon} a_{s,2}, \quad b'_{s,2} = \frac{1}{\varepsilon} (b_{s,2} + 1). \quad (\text{D3b})$$

The prefactors $\varepsilon^2/2$ and ε in Eqs. (D2a), (D2b) are not very important, because as a consequence of solving sec-

ular equations these basis functions will be effectively orthonormalized. Functions $R_{l,m}^{s,1}(r)$ and $R_{l,m}^{s,2}(r)$ have two important features. First, by a linear transformation the two functions, Eqs. (D2a), (D2b), can be transformed to two functions with the following radial dependencies

$$U_1(r) = \ddot{u}_s + a''_{s,1} u_s + b''_{s,1} \dot{u}_s, \quad (\text{D4a})$$

$$U_2(r) = \ddot{u}_s + a''_{s,1} u_s + b''_{s,1} \dot{u}_s, \quad (\text{D4b})$$

where the coefficients $a''_{s,1}$ etc. can be expressed through $a'_{s,1}$ etc. Since the functions $\ddot{u}_s(r)$ and $\ddot{u}_s(r)$ are linear independent, the same property applies to $U_1(r)$ and $U_2(r)$ and, consequently, to $R_{l,m}^{s,1}(r)$ and $R_{l,m}^{s,2}(r)$, although the property deteriorates as $\varepsilon \rightarrow 0$. Second, we still can impose the boundary conditions (18a) and (18b).

However, since the initial functions $R_{l,m}^{s,1}(r)$ and $R_{l,m}^{s,2}(r)$, have almost identical radial dependence (neglecting terms with $\varepsilon \ddot{u}_s$ and the others of high order of ε in Eqs. (D2a), (D2b) make them completely identical), the normalization procedure leads to the appearance of an effective basis state ϕ' , which is orthogonal to other basis states and expressed through the linear combination of initial states, $\phi' = C_1 \psi_{s,1} + C_2 \psi_{s,2}$ with large coefficients C_1 and C_2 (i.e. $|C_1| \gg 1$, $|C_2| \gg 1$). In that case, the partial charges of supplementary basis states can also be very large. Nevertheless, some of these partial charges are of opposite sign and effectively cancel each other in the final answer. We have observed the effect in the calculation of the hexagonal close packed lattice of cadmium reported in Sec. IV C.

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